Oleyl Alcohol From Animal Fats by Catalytic Reduction[1]

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Abstract

Catalysts effective in the selective reduction of methyl oleate or oleic acid to oleyl alcohol at 350 C and 3000 psi were Cr–Zn, Zn–Cd–Cu, Cr–Zn–Cd, Cr–Zn–Cd–Al and Zn-Cd-Al combinations. By-products were hydrocarbons, ethers and an unchromatographable still residue.

Introduction

Oleyl alcohol is available in this country from the saponification of sperm oil and by selective reduction with hydrogen. These sources at present represent only limited commercial production and the sodium reduction process, another alternative, has been abandoned as uneconomical. Large scale manufacture of tallow alcohols, with the usual copper chromite catalyst, is nonselective, causes hydrogenation at the double bond as well as reduction and produces only saturated alcohols, principally hexadecanol and octadecanol. Saturated long chain alcohols can be produced also by ethylene polymerization, in a selected range of molecular weight.

In contrast oleyl alcohol is a unique long chain monounsaturated alcohol available only from natural sources. Oleyl alcohol has many established uses (3) and many more potential uses which could be realized it were more readily available on a large scale. In rticular oleyl alcohol is an intermediate for biodegradable detergents. Sodium oleyl sulfate (11), unlike the saturated counterpart sodium octadecyl sulfate, is easily soluble and therefore more generally useful in different types of surface active and detergent applications for household or industrial use. Because of the importance of oleyl alcohol in the utilization of animal fats, possible improvement was sought in the reduction process. Other recent investigations of catalytic reduction with retention of unsaturation, have been those by Bertsch et al. (1,2), Pantulu and Achaya (7), Richter and Van den Berg (8) and Stouthamer and Vlugter (10).

The principal factors to be investigated were the choice of raw material (tallow, methyl oleate or oleic acid), reaction conditions (temperature, pressure, time) and in particular the selection of the catalyst. Laboratory experiments showed the reaction conditions could be in the range 10–150 min at 250–400 C and 2500–3000 psi but were most generally favorable in 60 min at 350 C and 3000 psi. The catalysts were mainly binary, ternary and quaternary systems based on certain combinations of Cr, Zn, Cd, Al and Cu. Catalysts were prepared in different forms in the laboratories of Swift & Co. or by the supplier.

One of two initial phases of our research verified the usefulness of sodium oleyl sulfate in detergent formulations (4). Another led to a chromatographic analysis for the reaction products (5). With methyl oleate as the substrate, for example, this method gave ıltaneous analysis for saturated and unsaturated ester, alcohol and hydrocarbon.

Experimental Procedures

Substrate

After initial experiments showed that high purity was not a decisive factor, the starting materials used were a bleachable, fancy grade of tallow and a commercial oleic acid and the corresponding methyl ester. The methyl ester had the following analysis, %: 0.8 $C_{14:0}$, 0.4 $C_{14:1}$, 1.3 unknown, 4.3 $C_{16:0}$, 5.1 $C_{16:1}$, 1.3 $C_{18:0}$, 77.4 $C_{18:1}$, 7.9 $C_{18:2}$, 0.3 C_{18}, 1.2 $C_{20:0}$.

Catalyst Preparation

Catalysts were supplied by Nopco Chemical Corp., Drew Chemical Corp. and Davison Division of W. R. Grace & Co., or were prepared in the laboratories of Swift & Co. Catalysts were prepared as outlined in the patent cited (9) or by one of the following methods.

Method A. Chromium trioxide and the acetates of other metals were dissolved in about 500 ml/mole of hot distilled water, evaporated to a paste, dried at 110 C and powdered and reduced in a stream of hydrogen, at the temperature shown in Table I.

Method B. The nitrates of all metals except Cr were dissolved in hot distilled water. In another vessel CrO_3 was dissolved in distilled water and concentrated NH_4OH, 170 ml/mole CrO_3, was added slowly. The nitrate solution was added to the chromate solution, NH_4OH was added to the mixture, the precipitate was settled, filtered, washed, dried at 110 C, calcined until the entire powder changed in color and then reduced in a stream of hydrogen.

Method C. Concentrated NH_4OH was added to a solution of CrO_3 in distilled water until the solution was neutral to litmus. The neutral solution was added to a hot stirred solution of Na_2CO_3 (slight excess). A solution of the nitrates of the other metals was added also. The mixture was cooled, the precipitate was filtered, washed, dried, calcined to a powder and reduced.

Method D. The metal nitrates were dissolved in hot distilled water (500 ml/mole) and slowly added to a stirred solution of excess Na_2CO_3. The mixture was cooled and filtered and the residue was washed, dried at 110 C, and reduced.

In all four methods catalyst reduction in a stream of hydrogen was carried out in a Vycor tube heated in a Lindberg heavy duty furnace at the temperature shown in Table I.

Catalytic Reduction With Hydrogen

A 1 liter Magne-Dash stainless steel autoclave was charged with 300 g of the ester, glyceride or acid and 30 g of catalyst, and nitrogen was swept through several times. The mixture was heated to the desired temperature, stirring was stopped and nitrogen was replaced by hydrogen to the desired pressure. Agitation was resumed and hydrogen was replaced when the pressure fell 100 psi. At the end of the reaction period the autoclave contents were cooled rapidly to 50 C and pressure was released. Methanol, water and hexane were added in small amounts to facilitate catalyst separation by centrifugation. Solvent and easily volatile products were removed in a rotary vacuum evaporator and the reaction product was analyzed by gas liquid chromatography (GLC). Results are shown in Table I.

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TABLE I

Reduction of Methyl Oleate, Tallow and Oleic Acid to Oleyl Alcohol
(Catalyst 10% by weight of substrate, 1 hr at 350 C and 3000 psi)

Expt. No.	Substrate	Catalyst composition,[a] Mole %					Catalyst reduction temperature, C	Reaction,[b] %	Selectivity[c]
		Cr	Zn	Cd	Al	Cu			
1	Methyl oleate	0	33	33	0	34	250	99	3.0
2[d]	Methyl oleate	0	33	50	0	17	250	75	17.4
3[e]	Methyl oleate	0	48	41	0	11	250	72	14.5
4	Methyl oleate	2	33	33	32	0	400	98	6.1
5	Methyl oleate	10	10	10	70	0	400	99	7.2
6	Methyl oleate	12	47	41	0	0	250	91	4.1
7	Methyl oleate	25	25	25	25	0	400	98	5.2
8	Methyl oleate	33	33	32	2	0	450	98	3.2
9	Methyl oleate	44	54	0	2	0	450	95	15.0
10[f]	Methyl oleate	50	50	0	0	0	250	98	14.8
11	Tallow	2	33	33	32	0	250	96	1.8
12	Tallow	10	10	10	70	0	250	99	1.0
13[g]	Tallow	25	25	25	25	0	250	99	2.0
14	Tallow	33	33	34	0	0	250	94	1.4
15	Oleic acid	2	33	33	32	0	350	99	7.2
16	Oleic acid	10	10	10	70	0	250	92	2.8
17	Oleic acid	25	25	25	25	0	250	99	6.1
18[g]	Oleic acid	25	25	25	25	0	350	98	7.8
19	Oleic acid	33	33	34	0	0	250	100	7.7

[a] Catalyst prepared by Method C except as noted.
[b] Based on recovered methyl oleate.
[c] Selectivity: per cent reduction/per cent chain saturation.
[d] Catalyst prepared by Method D. Reaction temperature 250 C.
[e] Catalyst prepared by Drew Chemical Corp. according to British Patent 792,896 (Ref. 9). Reaction conditions 300 C, 2500 psi.
[f] Catalyst prepared by Method B.
[g] Catalyst prepared by Method A.

Gas Liquid Chromatography

Product analysis was carried out on an F & M Model 810 gas chromatograph with dual column oven and dual hydrogen flame detector. The column was 6 ft × 4 mm i.d. containing 15% ECNSS-S (Applied Science Laboratories) on Gas Chrom P. After 3 min at 100 C, temperature was programmed at 6 deg/min. to 167 C and held there for the remainder of the run (5). Helium flow rate was 76 ml/min. Table II illustrates the analysis obtained.

By-products

Methyl oleate purity 93% (7% methyl linoleate) was used in an investigation of by-products, in an experiment with zinc chromite catalyst.

The reaction product, after removal of catalyst, was purified by passage through a falling film molecular still. The first pass (100 c/1 mm) removed hydrocarbons and methanol; the second pass separated product alcohol from starting material. Redistillation of the distillate from the first pass through a Podbielniak spinning band column gave a small amount of octadecadiene n_D^{25} 1.4530 [lit. value 1.4518 (6)], structure confirmed by Pt oxide catalyzed addition of four hydrogen atoms to give octadecane. Since IR spectra showed 30% *trans* double bonds it is reasonable to assume the presence of other position isomers besides the expected 1,9-octadecadiene. Small amounts of methyl oleyl ether and methyl octadecyl ether were also observed, identified by identical retention times with authentic samples.

Zinc chromite is a highly selective catalyst but one known to produce a large amount (about 50%) of unchromatographable by-product, concentrated in the still residue. Thin layer chromatography separated three fractions, molecular weight by vapor pressure osmometry 466, 462 and 362 (calculated for oleyl oleate 532). Infrared spectra showed the presence of *trans* unsaturation and of ester, hydroxyl and carboxylic acid functions but the fractions could not be further identified.

It is evident from Table II that compounds of less than 18 C atoms are present in the reaction product more than are present in the starting material. Some cracking apparently occurs in this catalytic process.

Discussion

Most of the experiments were exploratory to discover the best catalyst system in Cr-Zn-Cd-Al-Cu

TABLE II

Reduction of Methyl Oleate and Oleic Acid to Oleyl Alcohol[a]

Product	Analysis of reaction products by GLC			
	Methyl oleate		Oleic acid	
	1[b]	3[c]	8[b]	9[c]
Unknown, <18 C atoms	10.6	11.8	10.5	6.7
Octadecane	2.1	2.4	0.6	1.7
Octadecene	0.2	0.5		
Octadecadiene	7.0	8.6	12.6	13.1
Unknowns	2.8	3.9	3.2	4.3
Tetradecanol	6.8	7.0	4.2	5.1
Methyl palmitate	1.5	1.5	1.6	1.0
Methyl palmitoleate				1.0
Hexadecanol	6.6	6.4	5.0	6.7
Hexadecenol	5.1	4.2		
Methyl stearate	3.2	3.1	6.0	5.2
Methyl oleate	4.2	6.5	4.5	2.6
Stearyl alcohol	4.0	4.5	1.9	3.4
Oleyl alcohol	45.7	39.7	49.5	49.4
Yield of oleyl alcohol %[d]	62	56	68	66

[a] Experiments 4, 7, 15, 17 of Table I.
[b] Catalyst composition: 2Cr–33Zn–33Cd–32Al.
[c] Catalyst composition: 25Cr–25Zn–25Cd–25Al.
[d] Based on 77.4% methyl oleate or oleic acid and corrected for recovered substrate.

combinations with methyl oleate substrate. The highest selectivity in Table I is shown for Zn-Cd-Cu and Cr-Zn combinations. The Zn-Cd-Cu catalyst was most selective at lower temperatures, when formed by reduction at 250 C and used at 250–300 C, but reaction was less complete than usual (72–75%) and the product contained more unconverted methyl oleate. Higher catalyst reduction and reaction temperatures, than for experiments 2 and 3, increased the yield but decreased selectivity. This is the behavior to be expected with oleic acid, but is subject to confirmation. Zinc chromite, a highly selective catalyst, produced large amounts of unchromatographable by-product, from which further amounts of oleyl alcohol could be recovered after saponification. Properties were not improved by the presence of small amounts of Cd, Cu, Al or Ba.

Catalysts with selectivities which were not as high but which gave good yields of oleyl alcohol were Zn-Cd combinations with which Cr and Al could also be present. As shown in Table I Cr-Zn-Cd-Al systems were selective for the reduction of oleic acid but not for tallow.

Acceptable operating conditions may be with oleic acid as the preferred substrate for economic reasons, and either a Cr-Zn-Cd, Cr-Zn-Cd-Al, or Zn-Cd-Al catalyst formed by the acetate or carbonate-chromate method and reduced at 250 C or 350 C. As shown in Table II such catalysts can give a 60–70% yield of oleyl alcohol from a red oil grade of oleic acid. Selection of these catalysts is based on laboratory experiments which would need to be confirmed by further development at the pilot plant level.

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